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MEMORANDUM FOR PRS (In-House Contractor Publication)

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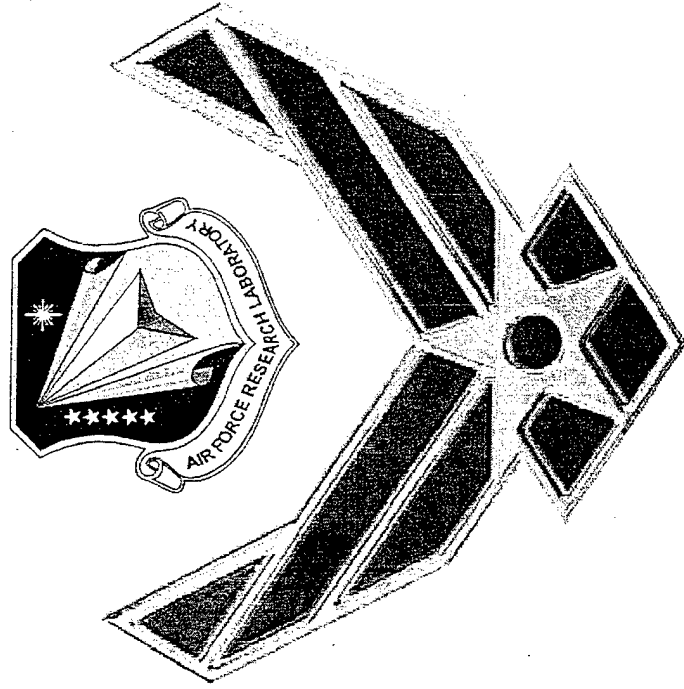
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Vij, Ashwani, "Matchmaking in Polynitrogen Chemistry: Search for Prospective Anions for
Combinations with N_5^+ "

(Statement A)

ACS National Meeting
(New Orleans, LA, 23-27 March 2003) (Deadline: **RUSH**, per RCC)

Matchmaking in Polynitrogen Chemistry: Search for prospective anions for combination with N_5^+



Ashwani Vij
Air Force Research Laboratory
PRSP
ashwani.vij@edwards.af.mil
(661) 275-6278

Award Symposium for Karl Christe, March 25-26, 2003
225th National ACS Meeting, New Orleans



Coauthors & Project Sponsors



Dr. Karl O. Christe,^{1,2} James G. Pavlovich,³ Vandana Vij,¹ Dr. Robert Corley,¹ Dr. William W. Wilson,¹ Dr. Fook S. Tham⁴

1. Air Force Research Laboratory, PRSP, Bldg 8451, 10 E. Saturn Blvd. Edwards Air Force Base, CA 93524
2. Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, CA 90089
3. Department of Chemistry, University of California, Riverside, CA 92521
4. Department of Chemistry, University of California, Santa Barbara CA 93106

**Dr. Michael Berman (AFOSR),
Dr. Arthur Morrish & Dr. Don Woodbury (DARPA),
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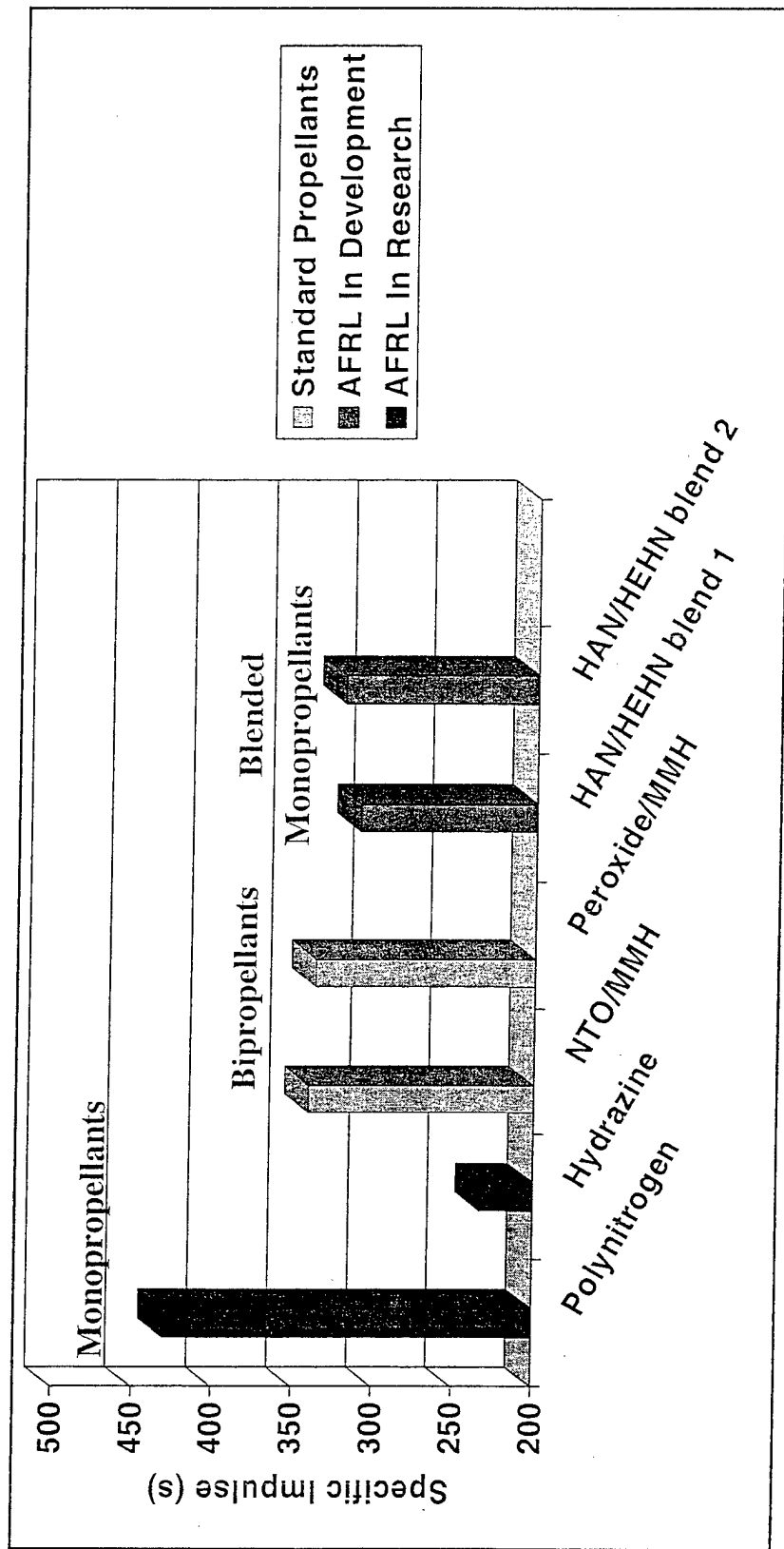
Why Polynitrogen Compounds ?



- Polynitrogen compounds contain only nitrogen atoms and are expected to have unusual properties. Most important among these are:
 - *High endothermicity*
 - *“Green” propellant*
- “combustion” product is only gaseous N_2
- *High density*
- *High I_{sp} values when compared to other monopropellants or bipropellants*
- *High detonation velocity*



Predicted Specific Impulse (s) Values for Neutral Polynitrogen Compounds





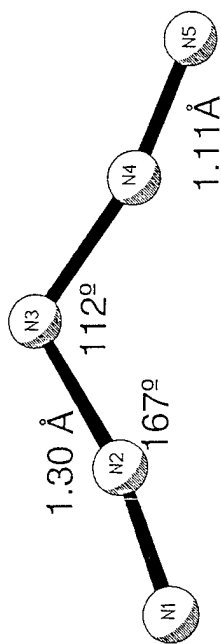
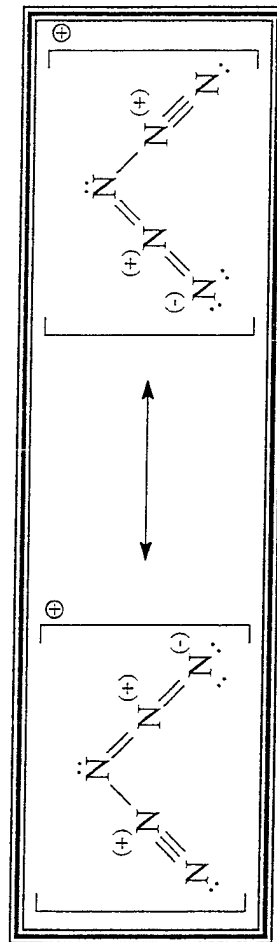
Synthesis and Properties of N_5^+



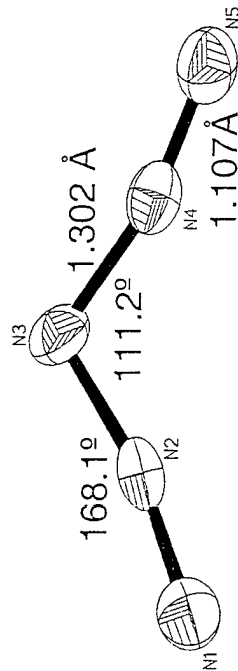
- First compound made was $N_5^+AsF_6^-$
 - ⇒ -78°C, 5 days, 60% purity, 50 mg scale
 - ⇒ Unstable at room temperature
 - ⇒ Exploded in low-temperature Raman spectrometer
- Second compound made was $N_5^+SbF_6^-$
$$N_2F^+SbF_6^- + HN_3 \longrightarrow N_5^+SbF_6^-$$
 - ⇒ First run: -64°C, 5 days, 80% purity, 300 mg scale
 - ⇒ Present method: Room temp., ½ day, 100% purity, 4 g scale
- Properties of $N_5^+SbF_6^-$:
 - ⇒ White solid
 - ⇒ Thermally stable to 70°C
 - ⇒ Survives impact sensitivity test (drop weight) at 150 kg/cm



Geometry of the N_5^+ Cation Predicted versus Experimental



Calculated Structure

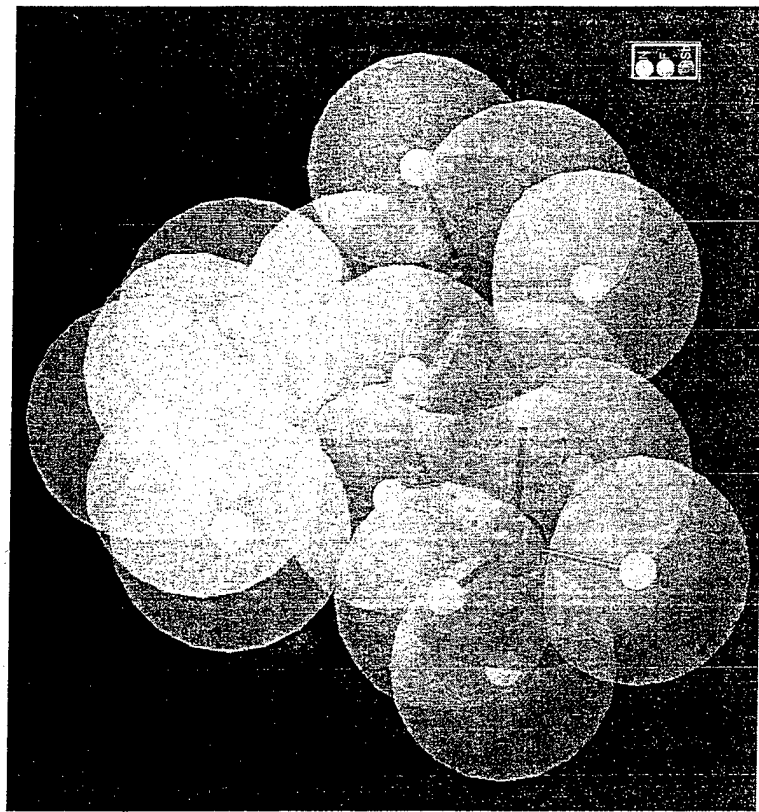


Experimental Structure

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Structure of the N_5^+ Cation



The Structure of $N_5^+Sb_2F_{11}^-$

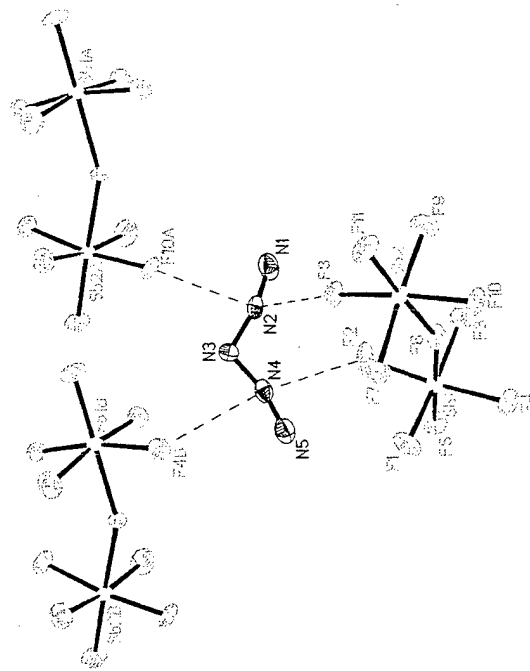
- ✓ The crystals grown from a mixture of SO_2 and SO_2ClF
- ✓ Crystal belong to the *Monoclinic* space group $C2/c$.
- ✓ Cell constants: $a = 10.913 \text{ \AA}$, $b = 12.654 \text{ \AA}$, $c = 16.675 \text{ \AA}$; $\beta = 104.72^\circ$
- ✓ $Z = 8$
- ✓ $R = 0.0678$

Inter-ionic Clipping!!

The N_5^+ cation fits into the $Sb_2F_{11}^-$ bend thus locking it, thereby precluding any possibilities of twisting



Crystal Packing Effects



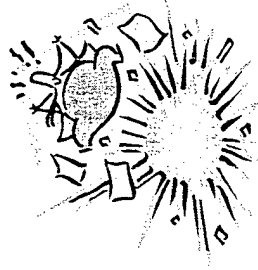
- ✓ The N...F Contacts support the resonance structure, where the N2 and N4 nitrogen atoms have a positive charge.
- ✓ N2 makes contacts at 2.723 and 2.768 Å; N4 contacts are at 2.887 and 2.814 Å



(In)Compatability of N_5^+



**Attempts to couple N_5^+ with energetic anions
can result in explosive reactions !!!**





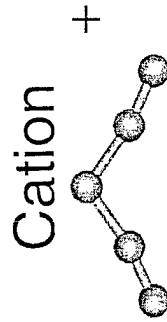
Recipe for Synthesizing Neutral Polynitrogen Compounds



- Combine a polynitrogen cation with a polynitrogen anion to form a neutral polynitrogen compound.



ONLY TWO STABLE POLYINITROGEN IONS KNOWN TO EXIST
IN BULK



N_5^+ cation

(discovered in 1999, AFRL, Christie)



N_3^- anion

(discovered in 1890, Curtius)

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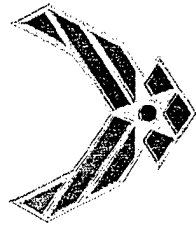
What Determines the Stability of a Polynitrogen Species?



Stability of a Polynitrogen Salt is Determined by
Thermodynamic and Kinetic Factors

Thermodynamic Factors

1. Electron Affinity of the Cation
 - A fixed value, if we aim for a N_5^+ salt, i.e., 10.5-11.5 eV
2. First Ionization Potential of the Anion
 - The azide ion has a very low value of about 2.1 eV, which is the main reason for the instability of $N_5^+N_3^-$
 - New polynitrogen anions are needed with higher first IP values. **N_5^- and N_7^- anions are most promising candidates**



What Determines the Stability of a Neutral Polynitrogen Species?



3. Lattice Energy of the Crystal

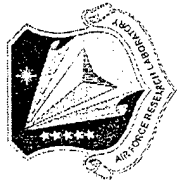
- U_L fixed by the molar volumes of cation and anion. Born-Haber cycle calculations for the lattice energy estimated for $N_5^+N_3^-$ are 50 kcal/mole lower than the requirement for the stabilization of an ionic salt

Kinetic Factor

- Activation Energy Barriers of the Ions Towards Decomposition
 - These energy values determine the stability of the individual ions



Polynitrogen for *Dummies* I



What has Thermodynamics and Kinetics

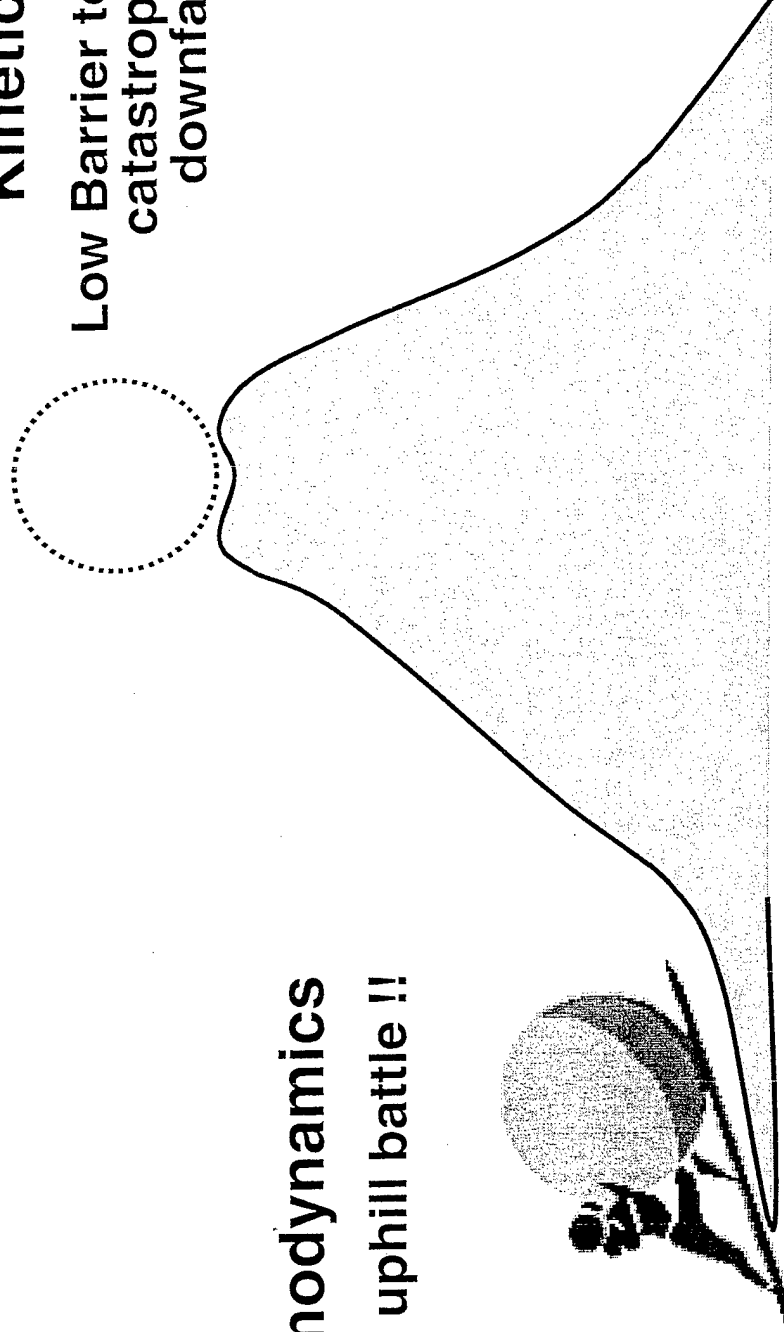
got to do with it ??

Kinetics

Low Barrier towards
catastrophic
downfall

Thermodynamics

It is an uphill battle !!

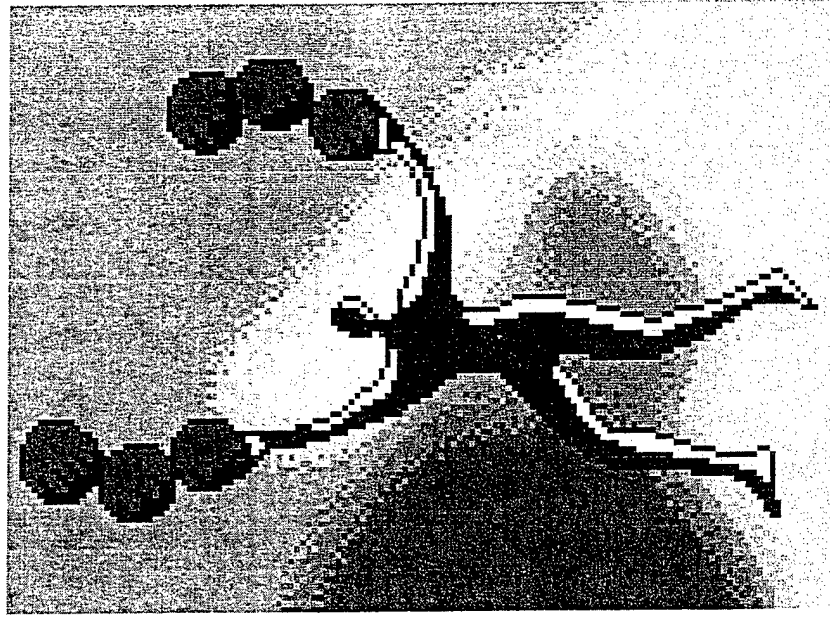




Polynitrogen for Dummies II



- Metastability requires a delicate balancing act !!



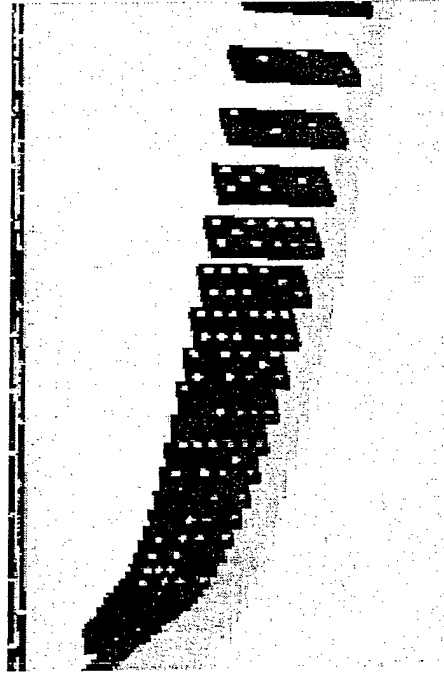
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Polynitrogen for *Dummies* III

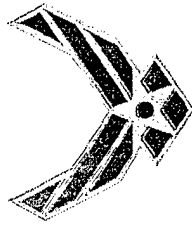


Avoid a domino effect !!!

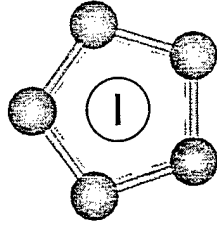
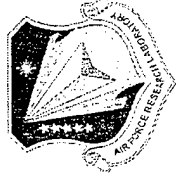


**Assembling a polynitrogen chain is like assembling metastable
dominos with perfect spacing, without prematurely triggering an
unwanted collapse**

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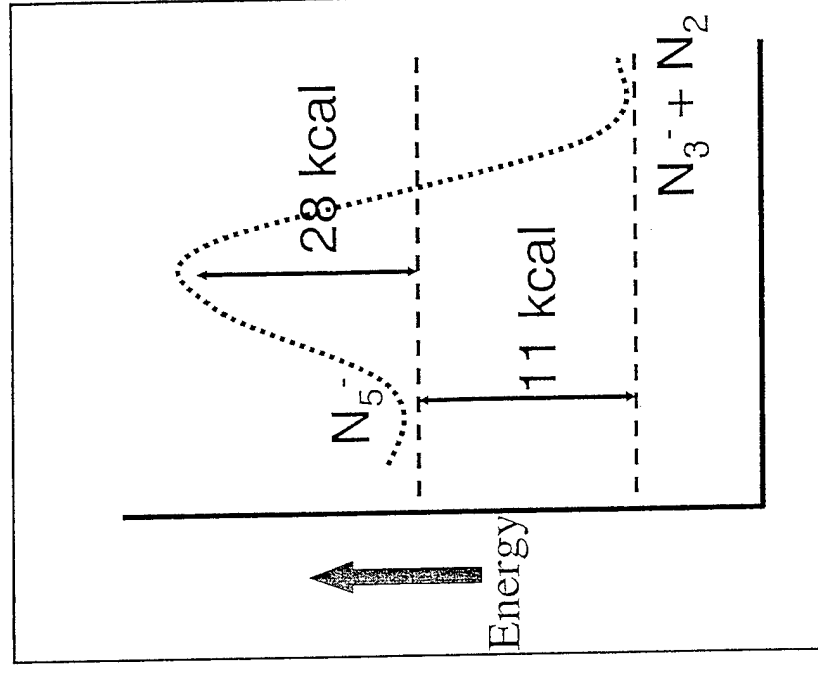


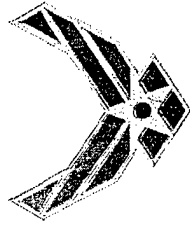
New Polynitrogen Anions as Counterparts for N_5^+



Pentazole anion (N_5^-)

- Theoretical calculations show that this anion has a 28 kcal/mole activation energy barrier for decomposition and its decomposition to N_3^- and N_2 is only 11 kcal/mol exothermic
- Aryl substituted pentazoles can be isolated as stable compounds only if stored at low temperatures. In methanol, these compounds rapidly decompose at room temperature to form aryl azides and N_2 gas



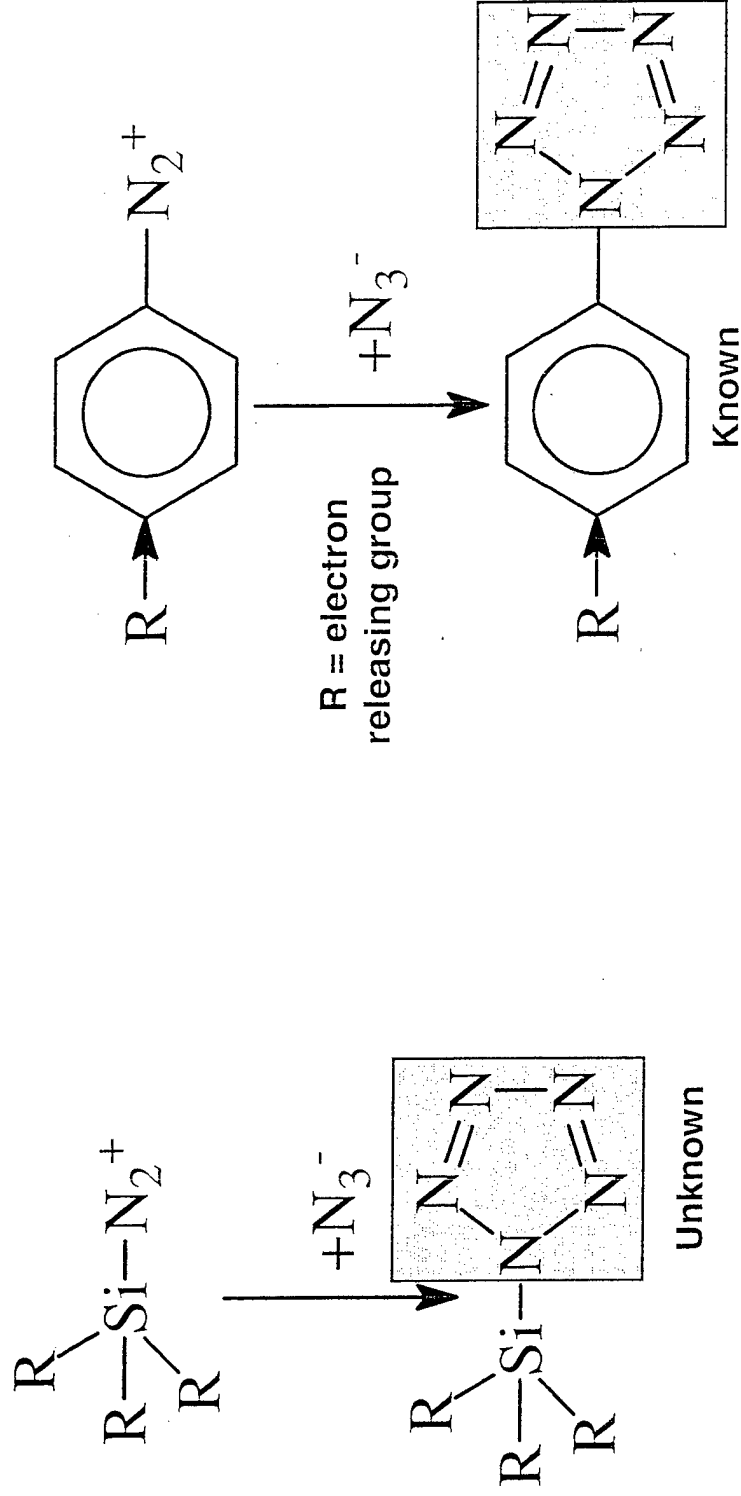
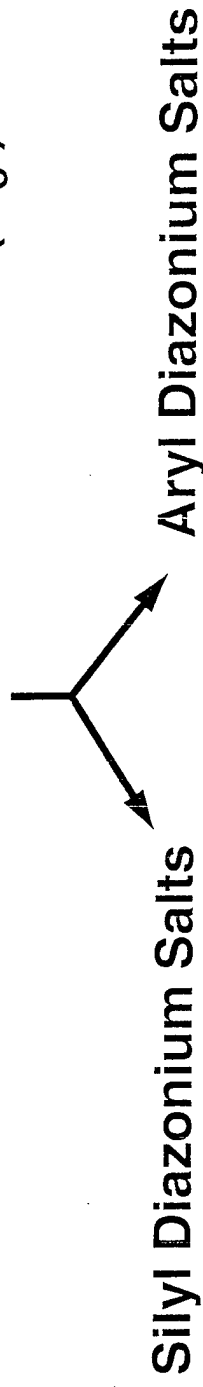


Synthetic Challenge – How do we make These New Anions??

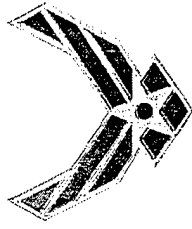


Synthesis of Substituted Pentazoles

Sources for the Pentazole Anion (N_5^-)



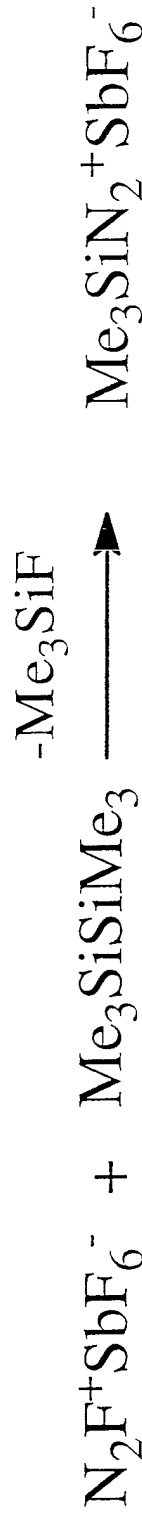
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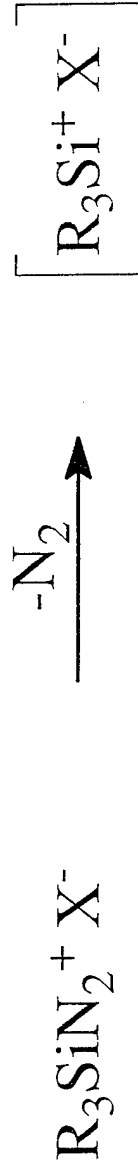
Formation and Stability of Silyl Diazonium Salts



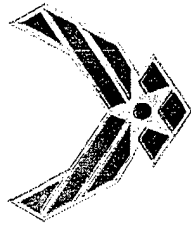
- Failed attempts to synthesize silyl diazonium salts



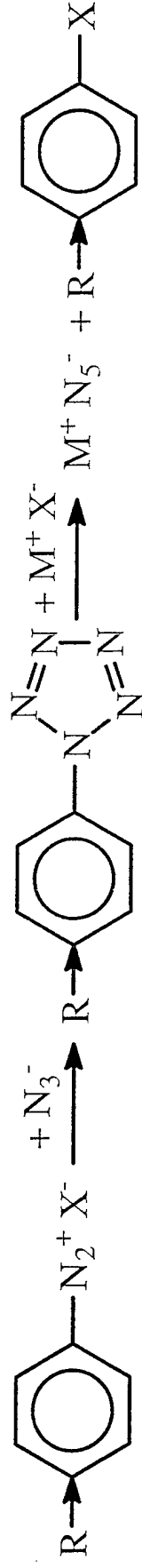
- R_3SiN_2^+ salts are unstable and spontaneously lose N_2



Theoretical calculations support this experimental observation

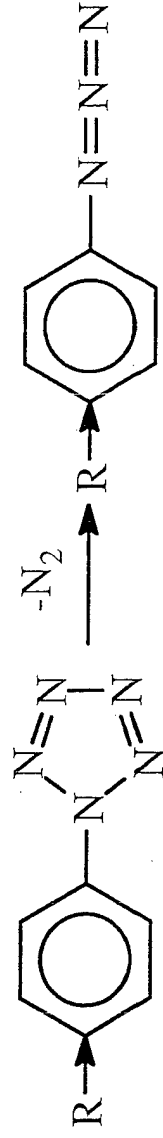


Use of Aryl Diazonium Salts – A Better Bet!



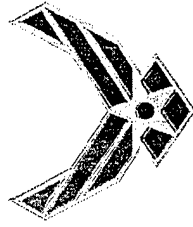
- R must be an electron releasing group, i.e., -NMe₂, -OH, -OCH₃, -OC₆H₅, -O⁻, etc.
- Some of these substituted arylpentazoles have been known for about four decades but **no success** had been achieved to cleave the N₅ ring from the aryl group

Aryl Pentazoles can rapidly lose N₂ at room temperature



I. Ugi, *Angew Chem.*, **1961**, 73, 172 and references therein

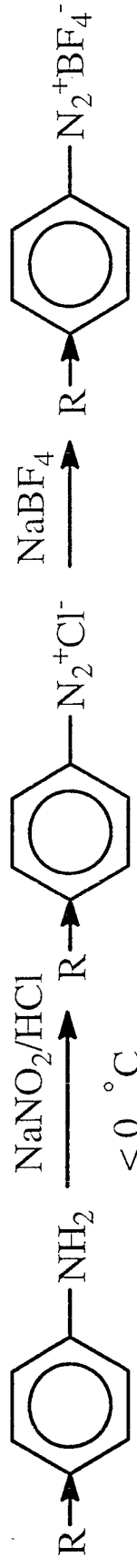
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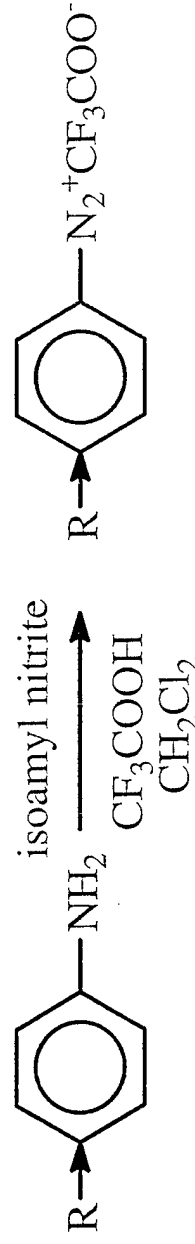
Synthesis of Aryldiazonium Salts



Aqueous Media



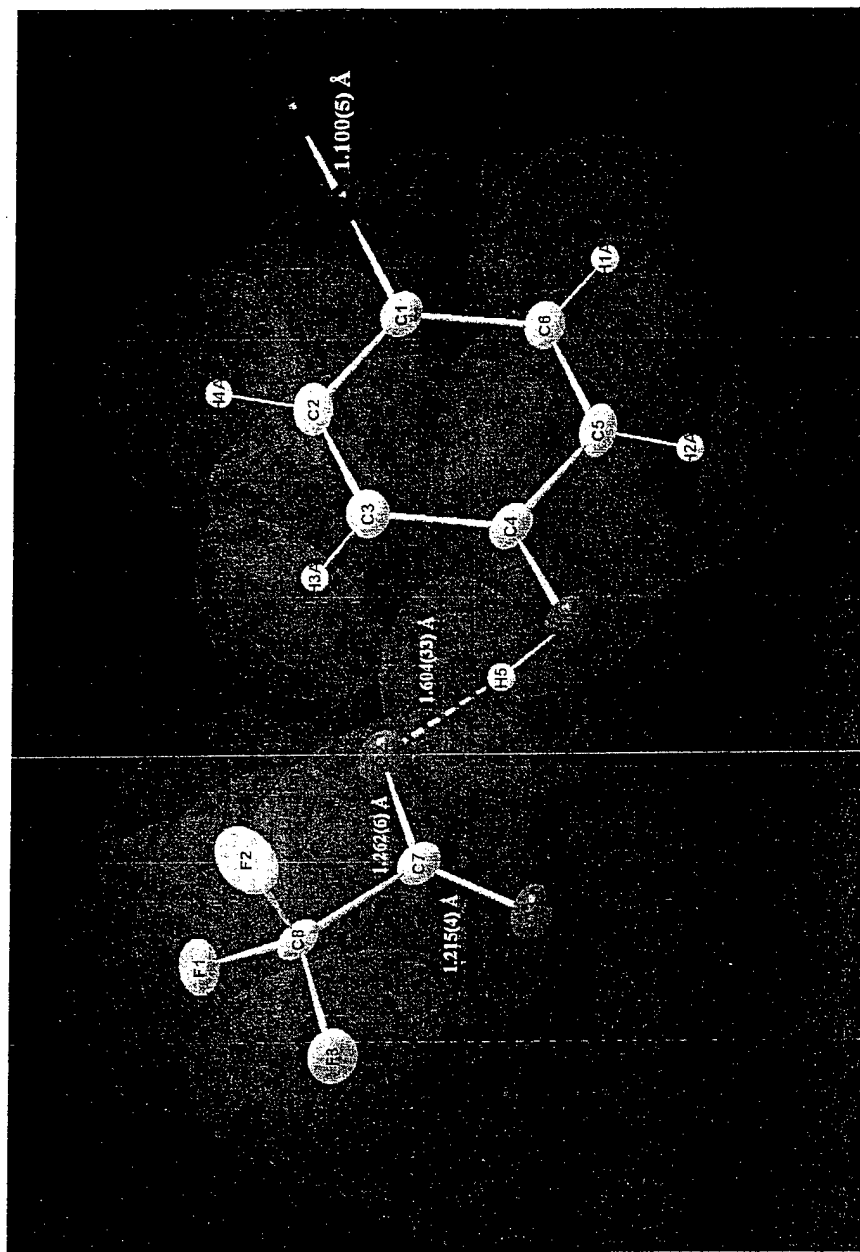
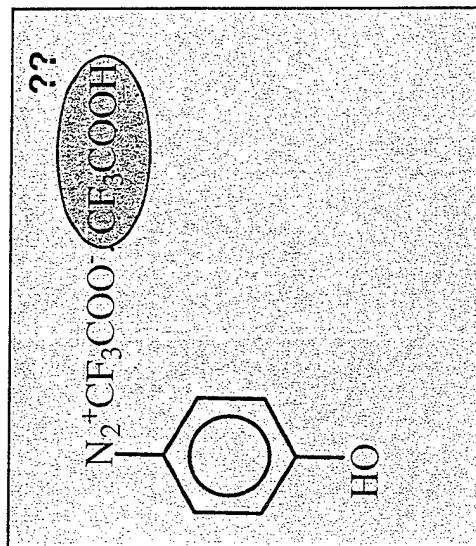
Non-aqueous Media

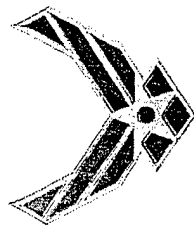


$\text{R} = \text{H}, \text{OH}, \text{OCH}_3, \text{OC}_6\text{H}_5, \text{OC}_6\text{H}_4\text{N}_2^+, \text{N}(\text{CH}_3)_2$

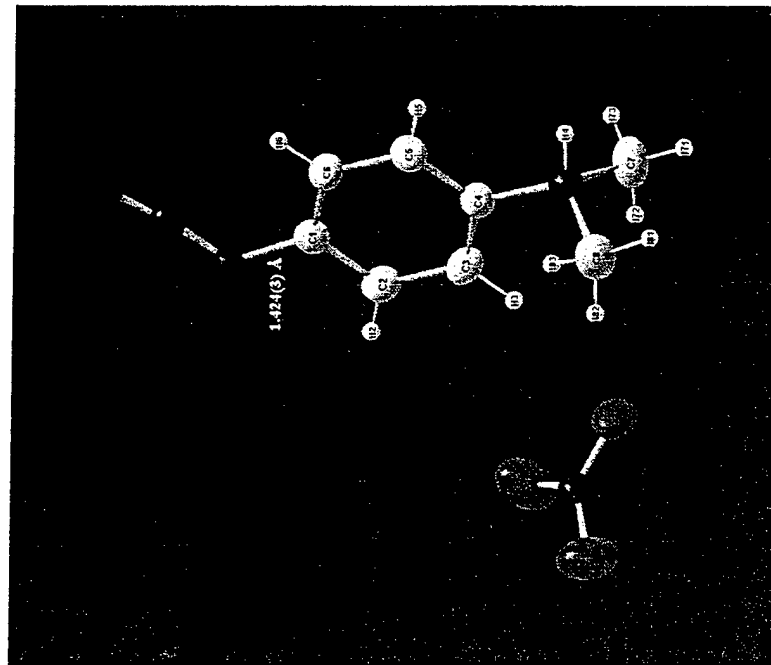
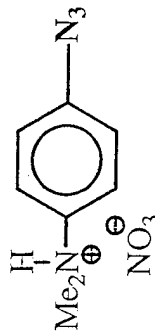
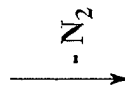
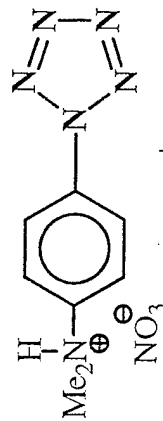
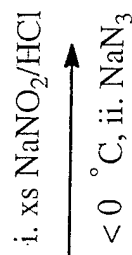
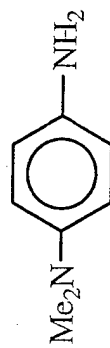


Colas and Goeldner, *Eur. J. Org. Chem.* **1999**, 1357-1366 reported the p-phenoxy diazonium salt to be a double salt. However, X-ray crystallography reveals no such stoichiometry.



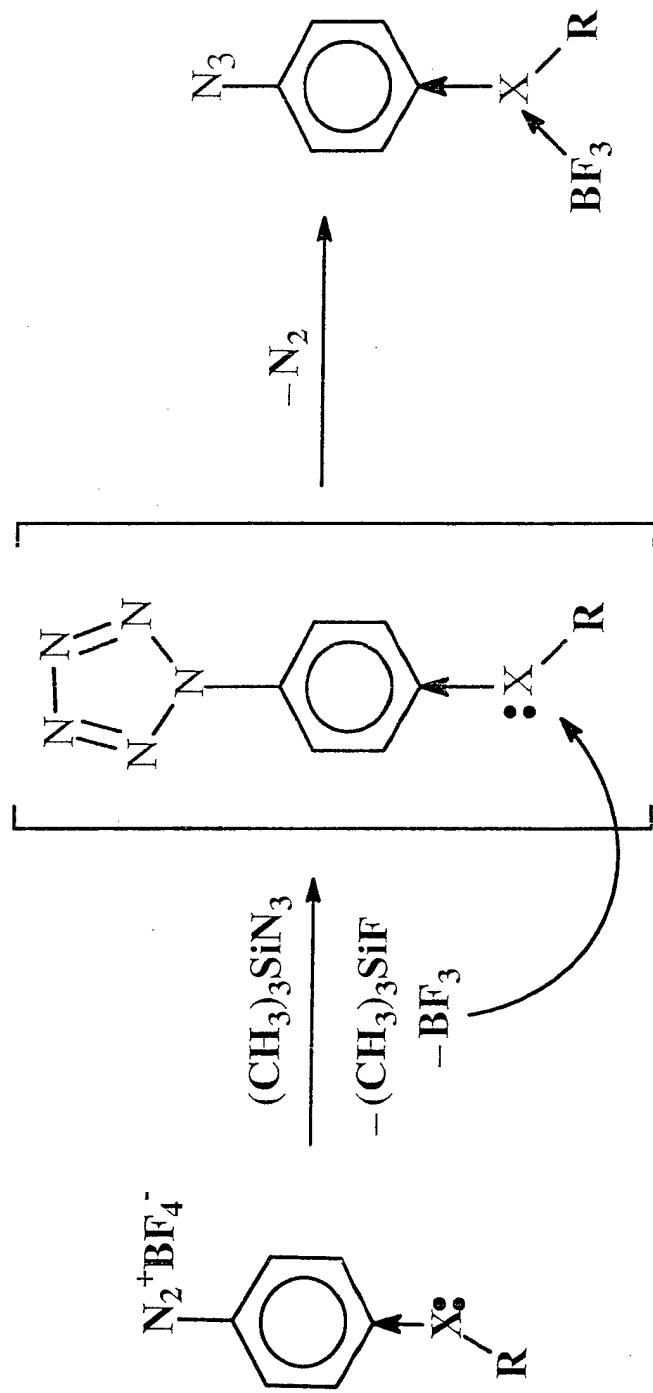
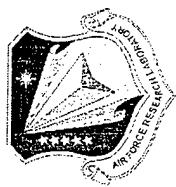


Role of the Lone Pair at Para Position





Reaction with Trimethylsilyl Azide

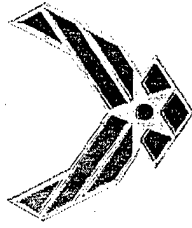


X= N, O

No pentazoles were isolated !!!

Reactions carried out in acetonitrile at -30°C

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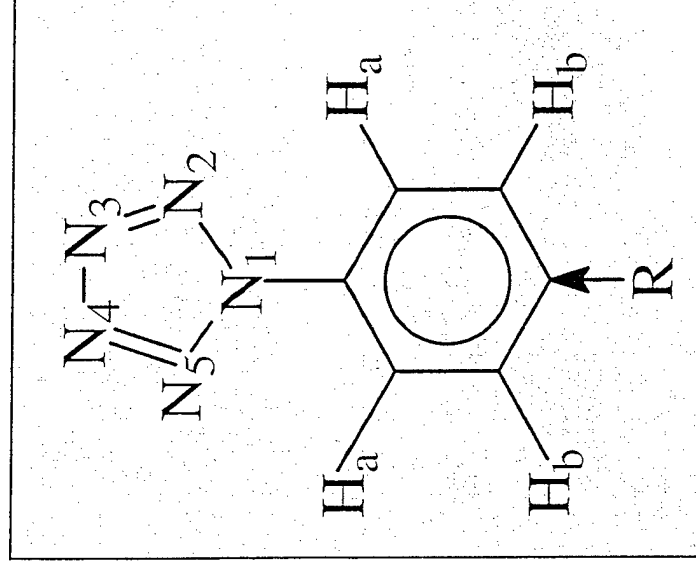


Identification of Arylpentazoles



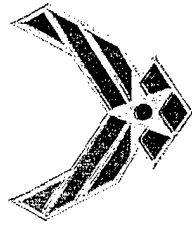
Pentazoles can be characterized by low temperature NMR spectral studies using ^{15}N labeled samples.

- ^1H NMR: AB-type spectrum with H_a and H_b at 8.0 and 7.0 ppm
- ^{14}N NMR: N_1 at ~ -80 ppm
- ^{15}N NMR: N_2/N_5 at ~ -27 ppm and N_3/N_4 at ~ -4 ppm



Note: Qualitative evidence for the presence of a pentazole ring: N_2 gas evolution in solution

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Cleavage of the Aryl-Pentazole Bond with Retention of the Pentazole Ring



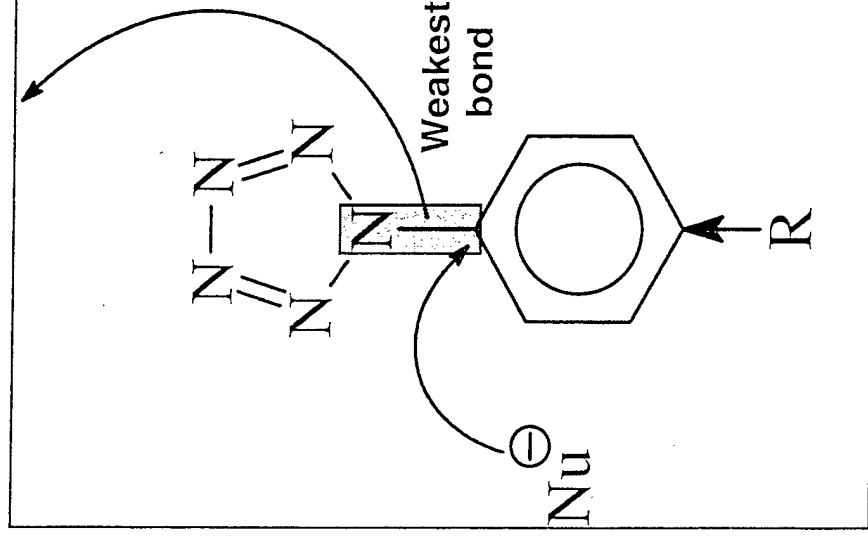
- **Chemical Methods**

- Ozonolysis does not work! (Ugi, Radziszewski)
V. Benin, P. Kszynski and G. J. Radziszewski, *J. Org. Chem.*, 2002, 67, 1354.

- Nucleophilic substitution using strong nucleophiles such as the OH^- , OR^- , F^- etc.

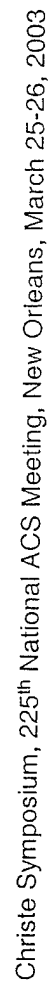
- **Collisional Fragmentation (ElectroSpray Ion Mass Spectroscopy – ESIMS)**

- Electrospray is very gentle and produces high concentration of the parent anion which can be mass selected
- Collisional fragmentation of the mass selected anions with variable collisional energies allow tailoring of fragmentation
- Negative ion detection eliminates interference from neutral or positively charged species



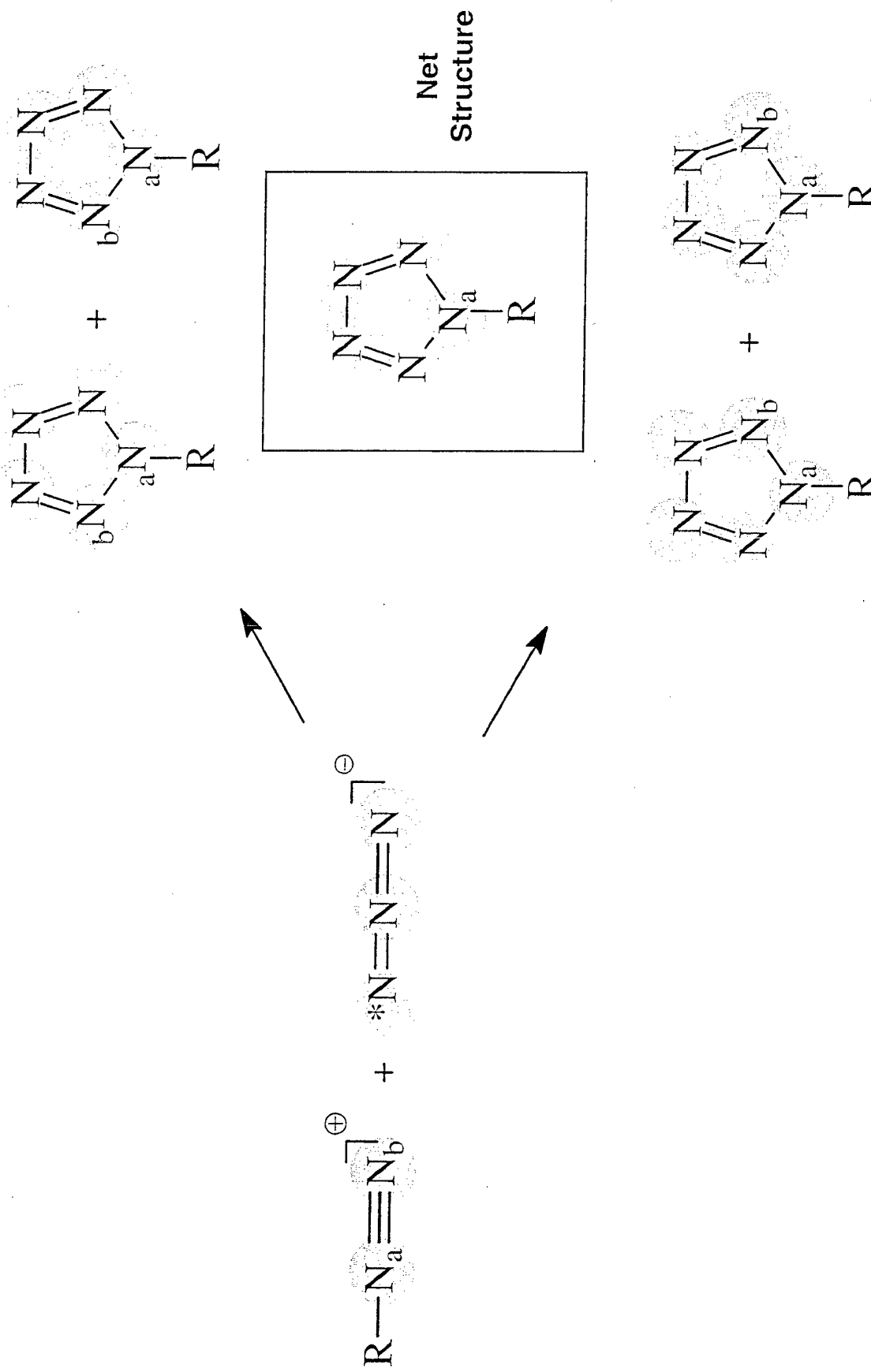


Observed peaks in the MSMS of 162





^{15}N Labeling of the Pentazole Ring

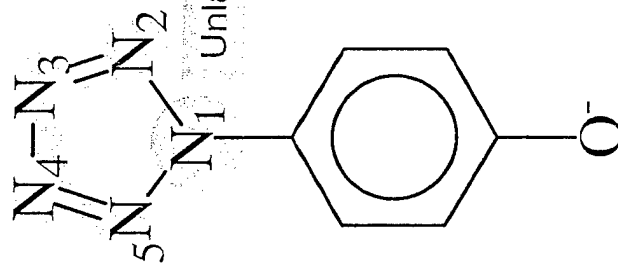




Is the Peak at m/e 70 indeed due to the Pentazole Anion???



^{15}N Labeled Pentazole

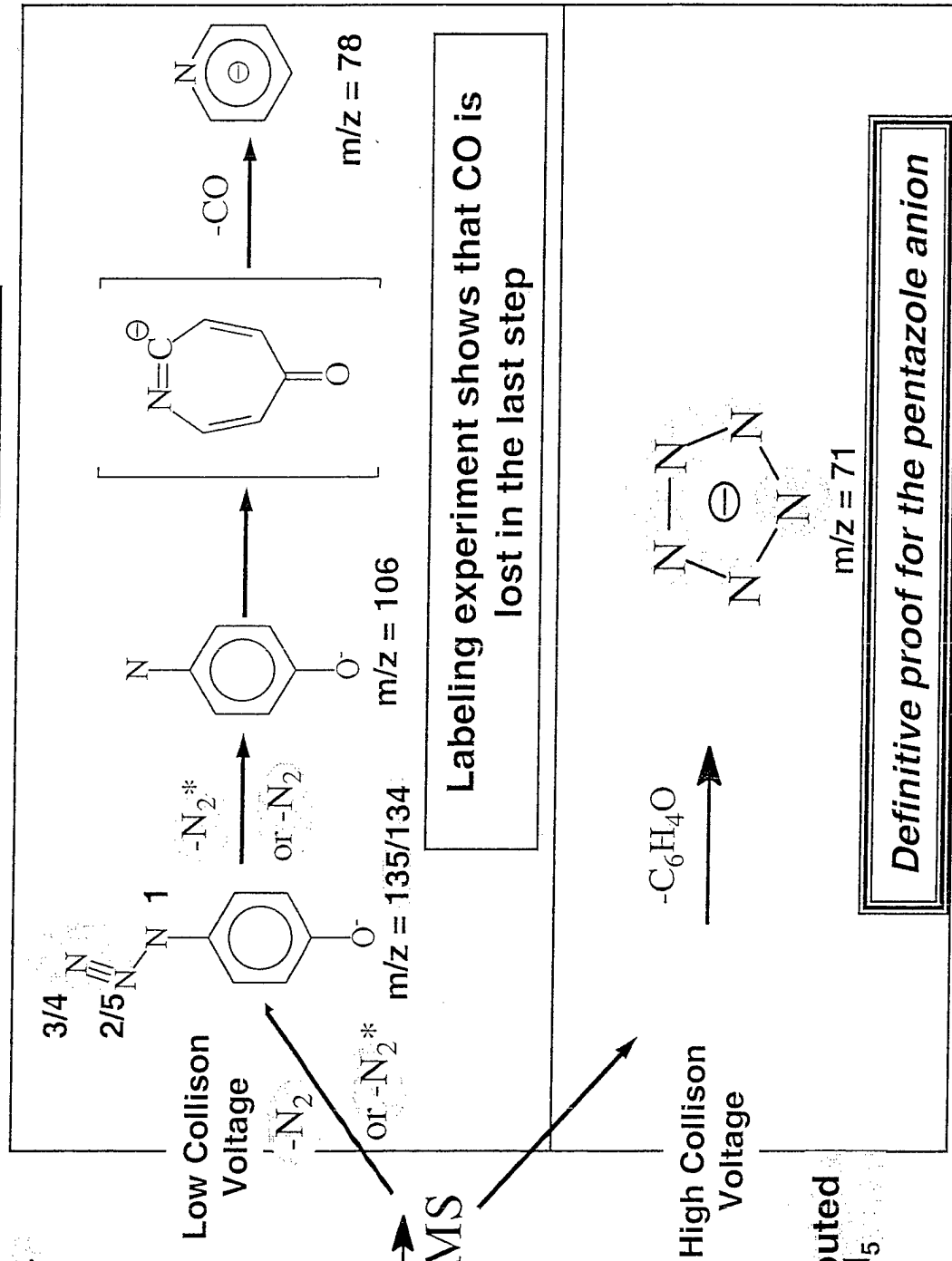


$m/z = 163$

^{15}N statistically distributed over N_2 , N_3 , N_4 & N_5

ES
MSMS

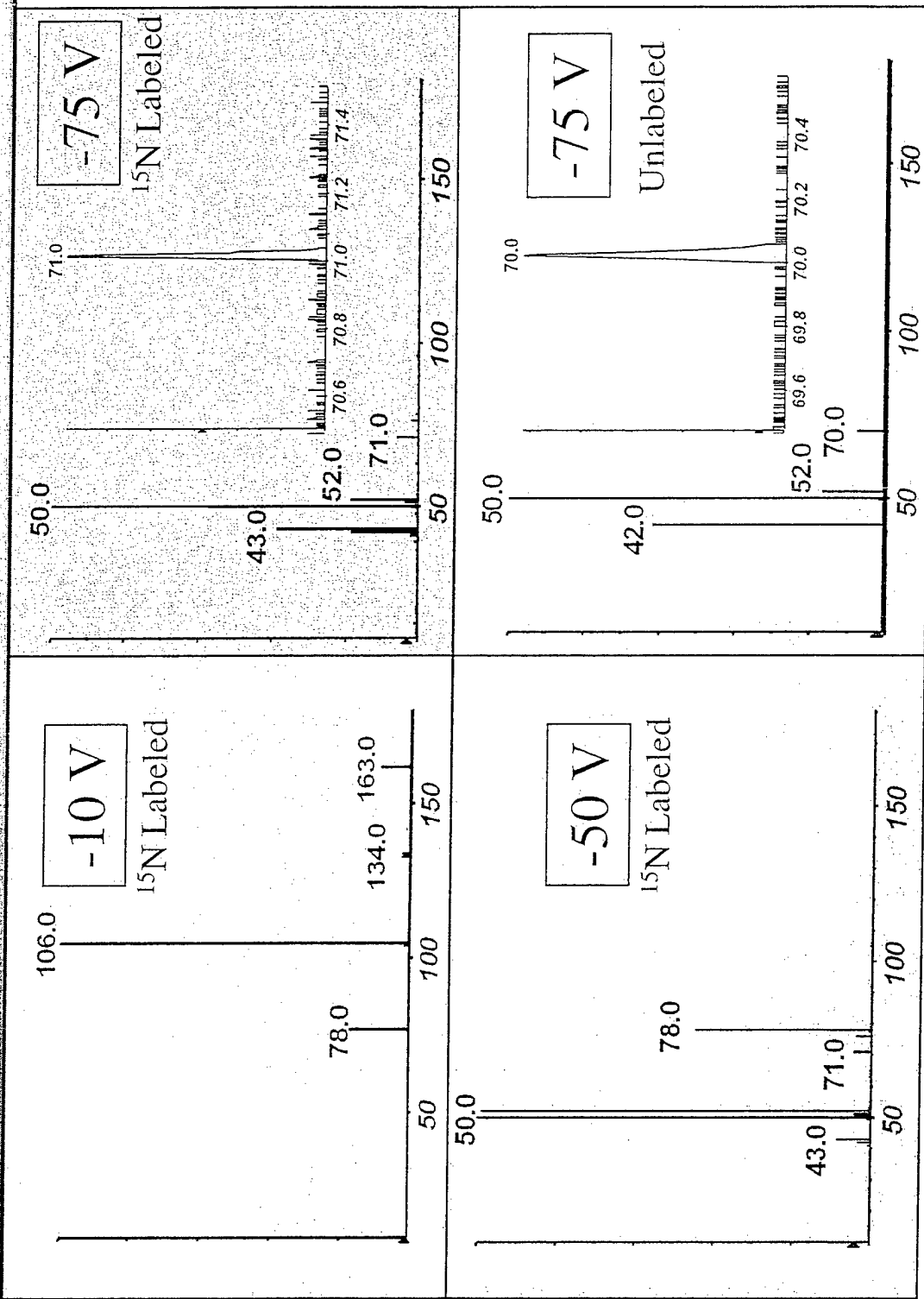
Observed peaks in the MSMS of 163



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MSMS of the Parent Ion Peak

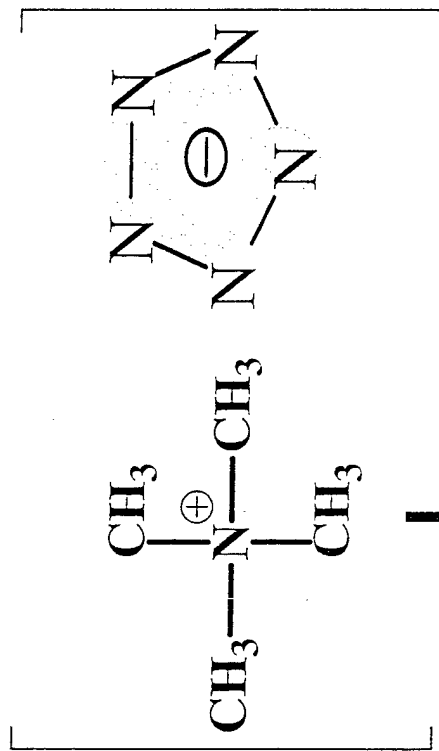
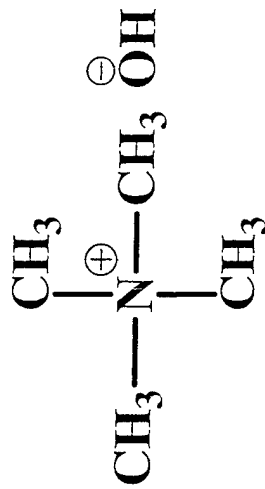
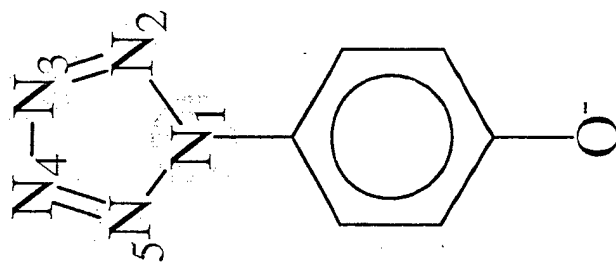


m/z

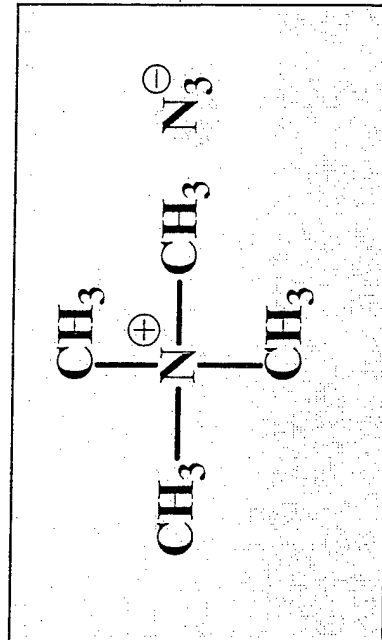
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Chemical Cleavage of the C-N Bond ?

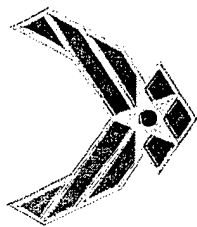


Not Isolated

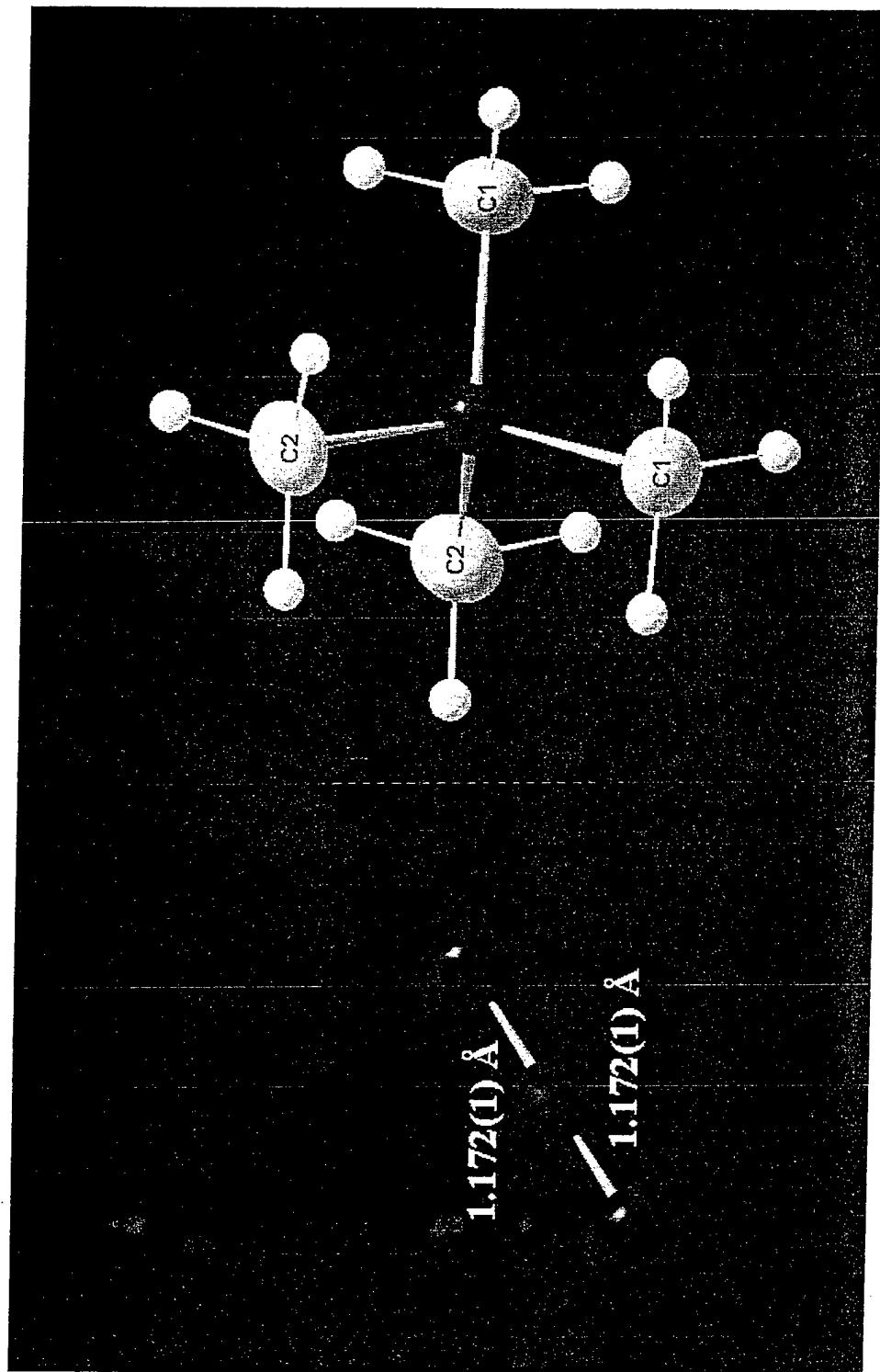


Formation of azide from decomposition of N_5^-

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Crystal Structure of Residue



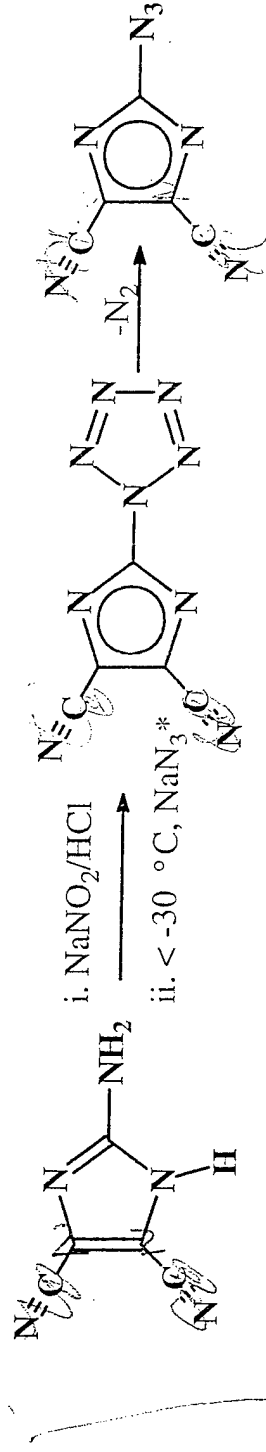
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Pentazoles with Heterocyclic Substituents

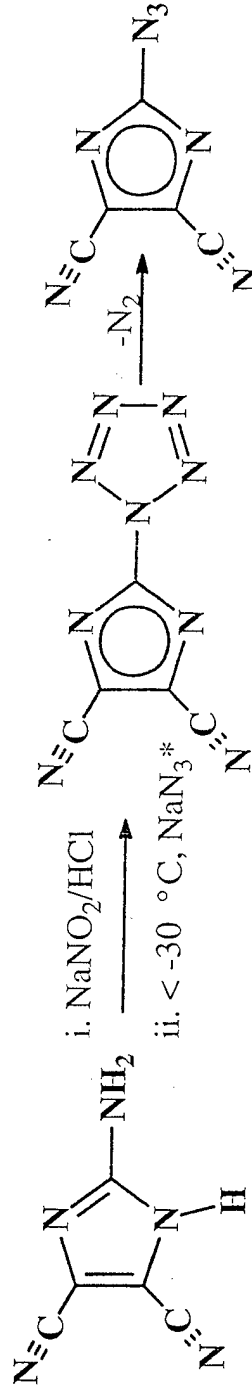


- These systems are unstable above -70 °C and the pentazole ring rapidly decomposes to liberate N₂ gas.



A. Hammerl and T. M. Klapoetke, *Inorg. Chem.* **2002**, 41, 906-912

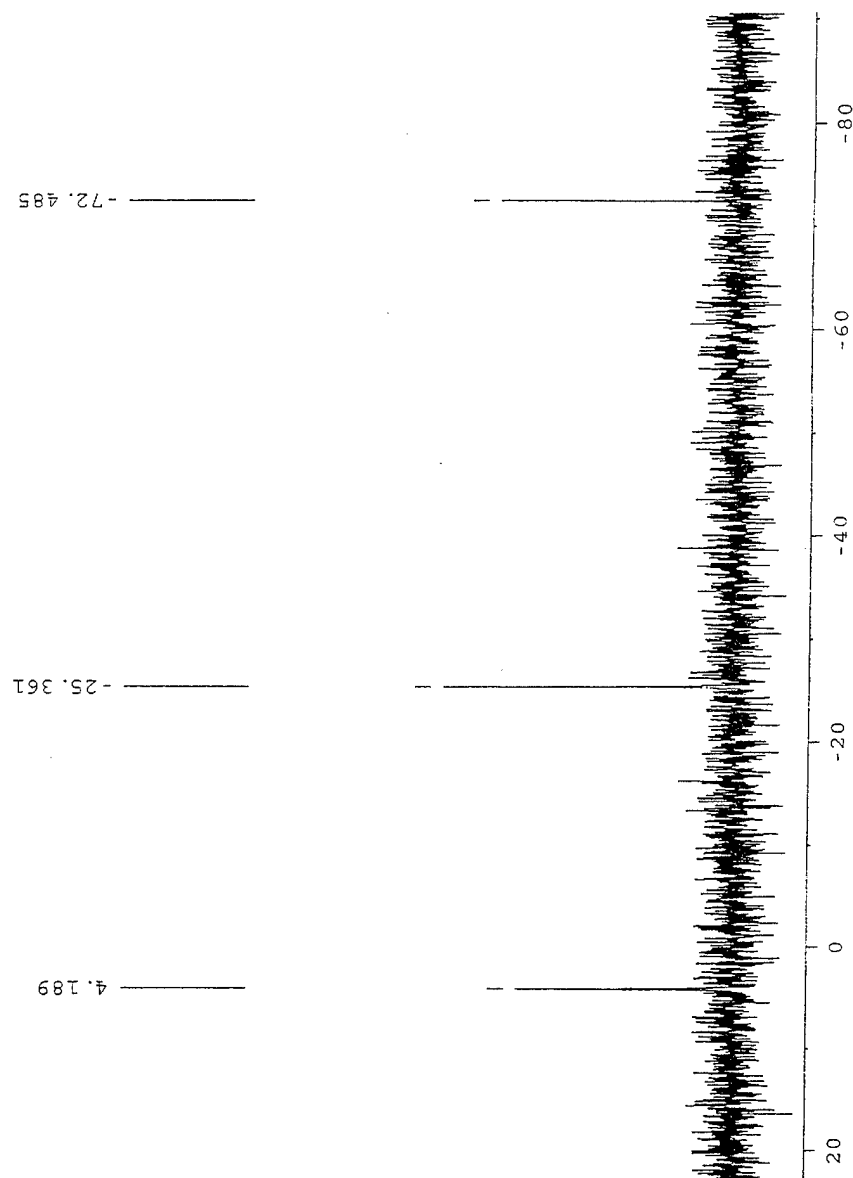
- Pentazole derived from 2-amino-4,5-dicyanoimidazole shows higher thermal stability



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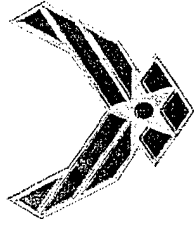


^{15}N NMR of 2-amino-4,5-dicyanoimidazolyl pentazole



^{15}N NMR recorded in a mixture of methanol and acetonitrile at $-30\text{ }^{\circ}\text{C}$, nitromethane used as an external reference (0 ppm)

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Summary



- Synthesized aryl pentazoles: hydroxy group at the *para*-position on the aryl ring gives the best results.
- Demonstrated selective cleavage of C-N bond by ESIMS with retention of pentazole ring. Results confirmed studying ^{15}N labeled pentazoles.
- First experimental detection of pentazole anion
- Synthesis of pentazoles with a heterocyclic substituents
- Offers potential pathway for bulk synthesis of N_5^- salts